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24 November 2014

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Webb, A.J. and Bloor, D. and Szablewski, M. and Atkinson, D. (2013) 'Temperature dependence of non-linear electrical conduction behavior in a screen-printed multi-component nanocomposite.', in Nanotechnology (IEEE-NANO), 2013 13th IEEE conference on. , pp. 1115-1118. Proceedings of IEEE conference on nanotechnology.

Further information on publisher's website:

<http://dx.doi.org/10.1109/NANO.2013.6720833>

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Temperature Dependence of Non-Linear Electrical Conduction Behavior in a Screen-Printed Multi-Component Nanocomposite*

Alexander J. Webb, David Bloor, Marek Szablewski and Del Atkinson

Abstract— Nanocomposite materials are of growing applications importance in many areas, particularly touch sensitive surfaces. Here, current-voltage measurements were performed over a range of temperatures and static compressive loadings on a multi-component, screen-printed nanocomposite in order to understand the physical nature of the electrical transport behavior. A physical model, combining a linear percolative electrical conductance and a highly non-linear conduction, that is ascribed to field assisted quantum tunneling, was successful in describing the temperature dependence of the I-V. This provides a theoretical underpinning for conduction in such functional nanocomposites.

I. INTRODUCTION

Electrically conducting composite materials have been a focus of study for over 60 years.¹ In bulk form, they often comprise electrically conducting filler particles, like metal powders or carbon black, dispersed in an insulating matrix, such as rubber, or even materials like cement.² Traditionally, the conductivity of these materials has been described using percolation and effective media theories.³ At low filler particle fraction content, composites take on an electrical conductivity close to that of the bulk insulating material. This does not change significantly until the filler particle fraction reaches what is known as the *percolation threshold*. This threshold is the critical filler particle fraction that gives rise to the formation of direct electrical connections between filler particles through the whole body of the material. The composite then becomes electrically conducting at and above this threshold.³ While quantum tunneling is a factor in the behavior of such composites, the topic has become more complex in recent years due to the recognition of the importance of field assisted tunneling in some composite systems.^{4,5} This occurs in composites incorporating filler particles with nanoscale features which enhance local electric fields, and may be modeled by combining direct ohmic electrical connections between filler particles and internal field emission between filler particles.⁶ Touch sensitive pressure dependent electrically conductive composites are beginning to grow in importance for applications involving touch sensitive surfaces, especially when the composite is made as an ink and is used as a printed electronic component.⁷

This paper investigates the electrical conduction processes in a pressure sensitive nanocomposite system as a function of temperature in order to understand the temperature dependence of the conduction behavior for future applications and critically to develop a deeper

understanding of the electrical conduction mechanisms responsible for the pressure sensitivity in such complex nanocomposite systems. The analysis of the temperature dependent behavior is based upon a combination of linear and non-linear conduction processes, the latter being associated with the presence of quantum tunneling via internal field emission.

II. EXPERIMENTAL METHODS AND TECHNIQUES

The nanocomposite investigated here comprises acicular titanium dioxide needles (on average $1.6 \mu\text{m} \times 100 \text{ nm}$) with a semi-conducting antimony doped tin oxide surface coating and electrically insulating and approximately spherical (diameter $\sim 200 \text{ nm}$) titanium dioxide nanoparticles dispersed in an electrically insulating polymer, such as a polyvinyl resin like Polyplast Type 383, which is used as a binder.⁸ The constituents were mixed together to form a homogeneous suspension, that was then screen printed to create test device structures. Pressure sensitive test devices were made using a high temperature stability, low expansion, *macor* ceramic substrate. A conducting electrode was first prepared on the *macor* tile by thermally evaporating a 2 nm layer of chromium, followed by the evaporation of a 150 nm copper electrode. A layer of the nanocomposite was screen-printed directly on to this electrode to form the lower element of the device. The upper electrode comprised a complimentary *macor* tile, prepared with the same chromium and copper layers. The two tiles were brought into registry to form the complete device. A schematic diagram of the *macor* tiles and an image of the complete device are presented in Fig. 1 (a) and (b), respectively.

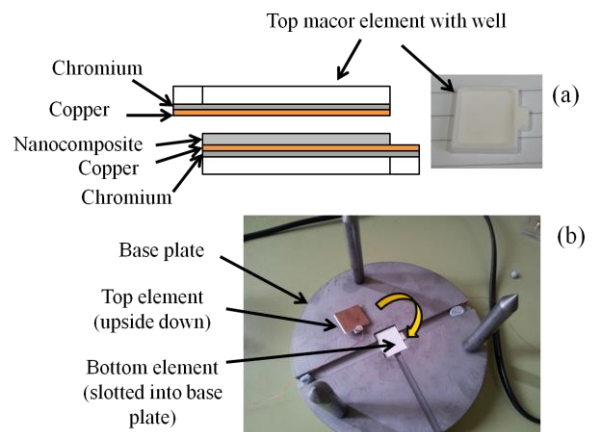


Figure 1. (a) Schematic diagram of the *macor* device. The top element has a machined well on the top surface for free weights to stand in, shown in the adjacent photograph. (b) Image of the device sitting in the base plate. The top element is shown upside down. The yellow arrow shows how the element is flipped over to sit on top of the lower element.

*Research supported by the EPSRC.

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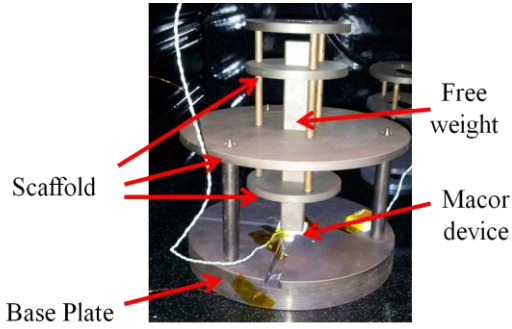


Figure 2. A picture of the complete custom compression rig in the oven, with the *macor* device under compression by a free weight.

The complete device sits within a custom-built compression rig, constructed from mild steel, which in turn was placed within a small oven. The electrically connected test device was placed into a shallow pit in the base plate of the rig, and free weights were placed on top of the device to apply compression to the nanocomposite. The compression vector was kept constant with a supporting scaffold. The high temperature test rig is shown in Fig. 2.

Current-voltage analysis was performed at a range of compressive loadings from 0.001 N up to 4 N and at temperatures ranging from room temperature up to 150 °C. For each measurement sequence at a selected temperature the device was exposed to a static compression and allowed to stabilize (the resistance of the device settles to a lower value after approximately 10 minutes, but here the samples were left for an hour). For the electrical measurements the voltage across the device was increased from 0 V to 10 V in 0.1 V steps over 5 seconds using a computer controlled Keithley 2420 sourcemeter. The voltage was then decreased back to 0 V at the same rate. This voltage sweep was repeated for 10 cycles. The temperature of the device was then raised by 10 degrees over 20 minutes. This routine of raising the temperature by 10 degrees and collecting I-V data was repeated up to 150 °C.

III. RESULTS AND DISCUSSION

First, examples of the electrical resistance response to compressive force at room temperature and 130 °C are shown in Fig. 3 (a) and Fig. 3 (b), respectively. The resistance falls rapidly with initial increases in compression and then falls further, but at a lower rate with increasing compression. This behavior can be described as two distinct regions. From 0.1 N to 1 N, the resistance of the nanocomposite drops sharply, whereas above 1 N the resistance change flattens, tending to a minimum value. The low force region (< 1 N) is of particular interest, as this is where the nanocomposite is undergoing initial compression and the I-V behavior is most non-linear. Above 1 N, the ink is largely compressed, and as such, the resistance plateaus.

It should be noted that the overall start resistance of the nanocomposite at 130°C in Fig. 3 (b) is approximately 10 times lower than that at room temperature in Fig 3 (a), although the form of the resistance change behaves in the same manner to compressive stress. I-V curves at room temperature and at compressions of 0.2 N and 0.8 N are

given in Fig. 4 (a) and (b), respectively. Both curves have a non-linear appearance, but the device at 0.8 N loading passed circa 5 times a greater current than at 0.2 N.

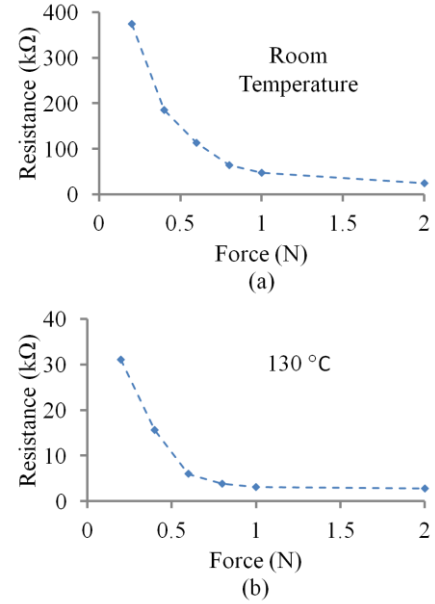


Figure 3. A plot of the resistance behavior with respect to compressive force at (a) room temperature and at (b) 130 °C.

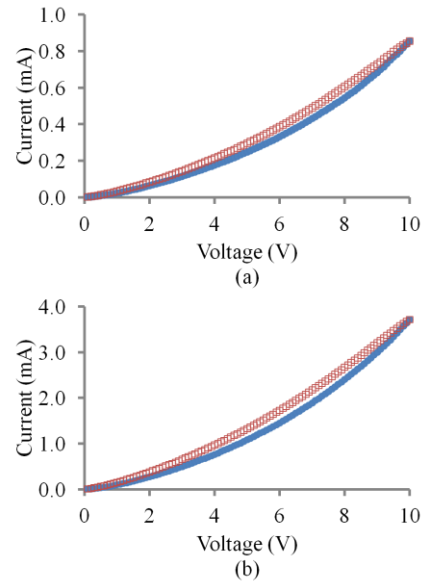


Figure 4. (a) I-V curve at 0.4 N compression and (b) I-V curve at 0.8 N compression. Both curves were obtained at room temperature. Solid blue circles are from the ramp up in voltage, open red squares are data from the ramp down. Error bars are smaller than the data points.

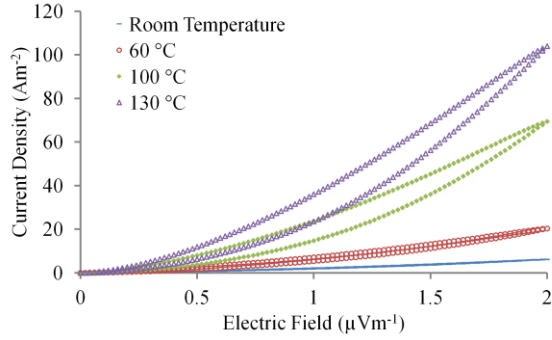


Figure 5. A plot of I-V curves taken at a static load of 0.6 N at four temperatures.

The I-V at a static loading of 0.6 N is shown at room temperature and temperatures ranging up to 130 °C. Fig. 5 shows that, as the temperature of the device is increased, the I-V behavior becomes more non-linear, and the device passes more current. The data from Fig. 5 and the lower start resistance evidenced in Fig. 4 suggests the material exhibits a negative temperature coefficient (NTC) of resistance and that expansion of residual polymer with temperature is unimportant.

The I-V also exhibit some hysteresis, caused by a lower nanocomposite electrical resistance upon the ramp down of the voltage, which becomes more pronounced at higher temperatures. The source of this hysteresis is under debate, but it is thought that it might originate from a combination of charge trapping effects and the NTC effect. Trap sites within the nanocomposite inhibit the current by trapping charge, but as they fill during the ramp up of voltage, the resistance of the material falls because they are no longer able to restrict the flow of current, and so more current is passed during the ramp down of voltage. Additionally, as the nanocomposite passes greater current under higher compressions and at higher temperatures, the material might experience joule heating, which would further decrease the electrical resistance due to the NTC effect, leading to the observed hysteresis.

The I-V characteristic is non-linear and is well modeled by a combination of ohmic percolative conduction, via direct electrical contact between filler particles, and quantum tunneling via internal field emission between filler particles, given in (1).^{9,10}

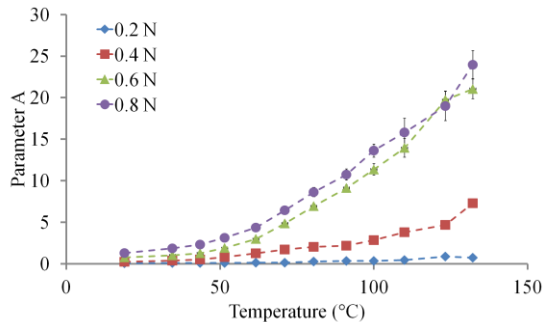


Figure 7. A plot showing how the parameter A behaves with increasing temperature, calculated here at the four compressive loadings indicated.

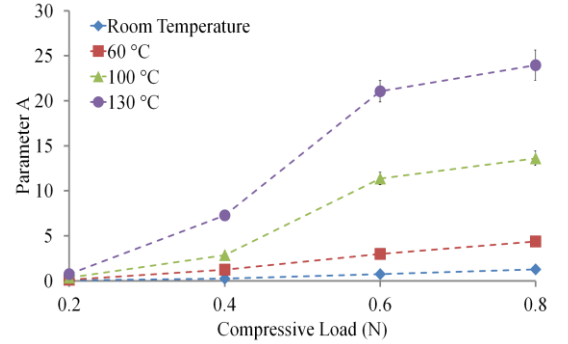


Figure 6. A plot showing how the parameter A behaves with increasing compressive load at 4 different temperatures.

$$J(E)_{\text{TOTAL}} = \sigma_0 E + AE^n \exp(-B/E) \quad (1)$$

Where $J(E)_{\text{TOTAL}}$ is the total current density passing through the nanocomposite, σ_0 is the linear conductivity, E the electric field, A is a parameter related to tunneling frequency and can contain several correction factors, n is an integer between 1 and 3, equaling 2 in the special case of Fowler-Nordheim tunneling, and B is a parameter related to the potential barrier height.

By fitting (1) to the I-V data, it is possible to extract a value for parameter A . Fig. 6 shows the behavior of parameter A with increasing compression. Parameter A initially increases at an increasing rate, from 0.2 N to 0.6 N of compressive loading. As 1 N loading is approached, the rate of increase begins to fall, coinciding with the plateau of electrical resistance in Fig. 3 (a) and Fig. 3 (b). At higher temperatures, the value of parameter A is, larger overall and the rate of increase between 0.2 N and 0.6 N becomes more exaggerated. Fig. 7 shows how parameter A varies with temperature when the nanocomposite is under static compressive loading. These data show that the parameter A varies in a non-linear manner with temperature, and that this non-linearity increases with increasing load.

If internal field emission is responsible for the non-linearity in the I-V data, the parameter A should follow a specific temperature dependence of the form shown in (2):¹¹

$$J(E)_{\text{IFE}} = D(\alpha T / \sin \alpha T) E^n \exp(-B/E). \quad (2)$$

Where D is a parameter containing numerous correction factors and other constants, such as the field enhancement factor, α is a constant and T is the temperature. Parameter A from equation 1 is equivalent to the term $D(\alpha T / \sin \alpha T)$.

A fit of (2) to the behavior of parameter A with increasing temperature, shown in Fig. 8, gives a good fit, suggesting the theory that internal field emission is a contributing conduction mechanism in the nanocomposite material.

IV. CONCLUSION

A nanocomposite material has been analyzed through electrical transport measurements in the form of temperature dependent I-V curves under different values of static compression. The nanocomposite has been found to exhibit two distinct regions of electrical behavior.

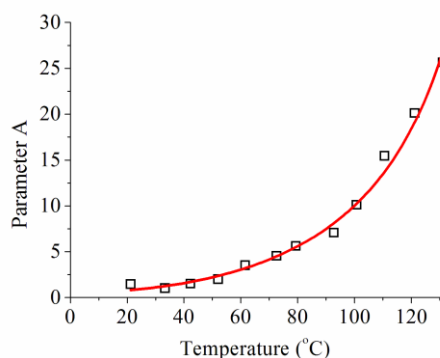


Figure 8. A plot showing the fit of equation (2) (solid red line) to the behavior of the parameter A with respect to temperature (open black squares).

Below 1 N of compressive loading, the nanocomposite undergoes physical compression and a dramatic decrease in electrical conductivity. Above 1 N, the electrical resistance tends to a minimum value. The I-V curves are non-linear and this behavior is exaggerated as the temperature of the device is increased. The I-V characteristic is well represented by a model combining linear, percolative electrical conductivity and a non-linear conductivity attributed to field assisted quantum tunneling. Both of these conduction mechanisms are sensitive to temperature and contribute to negative temperature coefficient of resistance. The temperature dependence of the I-V of this nanocomposite under low compression fits well to the temperature dependence of field assisted quantum tunneling.

ACKNOWLEDGMENT

All authors would like to thank Leon Bowen at the Durham Microscopy Facility.

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